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Theoretical condition for transparency in mesoporous layered optical media: Application to switching of hydrochromic coatings^{a)}

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Mesoporous Bragg stacks are able to change color upon infiltration or displacement of liquid compounds inside their porous structure. Reversible switching from transparency to coloration offers additional functionality. Based on Bruggeman's effective medium theory, we derive a transparency master equation, which is valid for bilayers of arbitrary host materials and pore-filling compounds. The transparency condition fixes pore volume fractions such that the effective refractive index is homogenized through the bilayer, hence, through arbitrary layered optical media built from this bilayer. This general concept is applied to the case of switching of hydrochromic coatings made of mesoporous mixed oxide Bragg stacks. © 2014 AIP Publishing LLC.

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Hydrochromic materials are porous materials whose color changes upon either infiltration or displacement of liquid compounds inside the porous structure. Remarkably, nature provides various organic templates of such materials,^{1–3} which in turns give inspiration for, e.g., novel humidity sensors.⁴ Generally, an intricate ordered porous multilayer structure, either exposed or buried, is involved with specific photonic crystal periodicity in one, two, or three dimensions. Not only water infiltration but also vapor condensation inside accessible pores of exposed structures can produce color changes as a result of the shift of the Bragg diffraction peak induced by refractive index modulation.^{2–4} Based on this principle, chemical sensors made of dielectric mesoporous Bragg stacks were exploited for organic vapor detection.^{5–11} The design of one-dimensional photonic crystals, so called Bragg stacks, is based on the Bragg diffraction law: $\lambda_B = 2\Lambda n_{\text{eff}}$ (λ_B : Bragg peak wavelength, n_{eff} : effective refractive index of a bilayer, Λ : spatial period, i.e., bilayer thickness). By suitably selecting layer thicknesses, porosities, and host materials with adequate refractive indexes, the Bragg peak is positioned in the visible range, producing a specific color, which then varies upon liquid infiltration or displacement.¹² Although this recipe has been applied many times, it has only been adapted recently for switching from transparency to coloration by tailoring porosities of adjacent layers in a mixed oxide Bragg stack.¹³ Indeed, transparency corresponds to the peculiar case in which the effective refractive index contrast between adjacent layers cancels out and, consequently, the photonic crystal behaves as an effective homogeneous, transparent material. In a more general perspective, effective index matching should be achievable for any mesoporous layered optical media with different pore filling compounds by suitably selecting the porosity in each layer. In this Letter, we theoretically derive a transparency master

equation, which must be satisfied by pore volume fractions (porosities) in a bilayer with arbitrary host materials and pore-filling compounds in order to make it transparent to electromagnetic radiation, at least in the wavelength range where host material and compound refractive indexes can be assumed to be constant. We apply this general concept to the switching of hydrochromic coatings from transparency to coloration (and vice versa) upon liquid infiltration or displacement. As an illustration, we report on the hydrochromic response of a mesoporous mixed oxide Bragg stack synthesized by sol-gel chemistry. The proposed transparency concept could be easily applied to any other oxide systems synthesized by chemical¹⁴ or physical¹⁵ methods.

Let us consider, a Bragg stack made of mesoporous oxide layers deposited on a transparent glass substrate. For the sake of generality, high-index (e.g., TiO_2) and low-index (e.g., SiO_2) layers are referred as L_1 and L_2 layers, respectively. Since pore sizes (mesopores) are much lower than visible-range wavelengths, Bruggeman's effective medium theory can be used to calculate ϵ_{eff} , the effective permittivity.¹⁶ According to Bruggeman's theory, ϵ_{eff} is the solution of

$$f_p \frac{\epsilon_p - \epsilon_{\text{eff}}}{\epsilon_{\text{eff}} + (\epsilon_p - \epsilon_{\text{eff}})L} + f_h \frac{\epsilon_h - \epsilon_{\text{eff}}}{\epsilon_{\text{eff}} + (\epsilon_h - \epsilon_{\text{eff}})L} = 0, \quad (1)$$

where f_p ($f_h = 1 - f_p$) is the pore (host material) volume fraction, $n_p = \sqrt{\epsilon_p}$ is the refractive index of the material filling the pores (air: $n_p = 1.00$ and water: $n_p = 1.33$), $n_h = \sqrt{\epsilon_h}$ is the host refractive index (TiO_2 : $n_{h,1} = 2.50$ and SiO_2 : $n_{h,2} = 1.50$), and L is the depolarization factor. The explicit solution of this second degree equation is (assuming spherical pores, i.e., $L = 1/3$)

$$\epsilon_{\text{eff}} = \frac{1}{4} \left(\beta + \sqrt{\beta^2 + 8\epsilon_h\epsilon_p} \right), \quad (2)$$

where $\beta = [(3f_h - 1)\epsilon_h + (3f_p - 1)\epsilon_p]$. When considering an arbitrary bilayer, noted (L_1, L_2) , transparency requires a

^{a)}This work is dedicated to our colleague and friend Professor J. P. Vigneron who died accidentally on 24th June 2013.

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theoretical condition that is defined by the relationship $f_{p,2} \equiv \zeta(f_{p,1})$ such that $\varepsilon_{\text{eff},1} = \varepsilon_{\text{eff},2}$. If this condition is fulfilled, any multilayer stack (not necessarily periodic) made of L_1 and L_2 layers behaves effectively as a homogeneous medium. If L_1 and L_2 host materials are optically transparent (dielectrics), the whole stack remains transparent to light, assuming constant refractive indexes over the wavelength range of interest. Mathematically, the transparency condition can be derived by writing (1) for layers L_1 and L_2 and then equating both expressions. By introducing the dimensionless variable $u = \varepsilon_{\text{eff}}/\varepsilon$ and the function $g(u) = (1-u)/[1+(1/L-1)u]$, the transparency condition can be expressed as

$$f_{p,2} = f_{p,1} \frac{g(u_{p,1}) - g(u_{h,1})}{g(u_{p,2}) - g(u_{h,2})} + \frac{g(u_{h,1}) - g(u_{h,2})}{g(u_{p,2}) - g(u_{h,2})}. \quad (3)$$

Although the relationship $f_{p,2} = \zeta(f_{p,1})$ is nonlinear (arguments of g functions actually depend on $f_{p,1}$ or $f_{p,2}$), we will see hereafter that transparency master curves are well approximated by linear dependencies in practical cases.

Assuming that pores can be either empty or completely filled with liquid (water), four configurations of the photonic crystal unit cell, i.e., (L_1, L_2) bilayer, exist *a priori* for which (3) can be satisfied (Fig. 1). At first glance, it appears easier to achieve transparency with empty pores in high-index L_1 layers and liquid-filled pores in low-index L_2 layers. Indeed, this configuration (Fig. 1, II) helps decreasing (increasing) effective index in L_1 (L_2) layers, hence, matching both indexes at some point. However, transparency can still be achieved in three other configurations by playing on porosities. Since the porosity can never be higher than unity, it may nevertheless happen that no combination of porosities exists allowing to achieve transparency: this is the case, for example, with water-filled pores in L_1 layer as far as $f_{p,2} > 0.33$ (Fig. 1, III). When the transparency state is defined by empty pores in both layers (Fig. 1, I) and in the limit (non physical) case where $f_{p,2} = 1$, one finds $f_{p,1} = 1$. This is logical since L_2 material, in this limit case, is actually air void and the only possibility to match the index in L_1 material is to have air void as well. A similar argument (with liquid replacing air) applies to the transparency state defined by

liquid-filled pores in both layers (Fig. 1, IV). On the other hand, when the transparency state is defined by empty pores in L_1 layer and liquid-filled pores in L_2 layer and in the same limit case as above ($f_{p,2} = 1$), we find that $f_{p,1} < 1$. Again, this is logical since L_2 material, in this case, is actually liquid and matching the liquid index (1.33 for water) can be obtained using a sufficiently large but less than unity fraction of empty pores in L_1 material.

Let us, now apply this general concept to the switching behavior of a mesoporous Bragg stack of N bilayers (L_1, L_2). We first assume that the transparent state (Ψ_T) is the one for which all pores in both L_1 and L_2 layers are empty, say $f_{p,1} = 0.72$ and $f_{p,2} = 0.30$ (Fig. 1, I). In practice, the Ψ_T state could be realized upon dry environment.¹³ The effective refractive index, common to both L_1 and L_2 layers, is then calculated from (1): $n_{\text{eff},1} = n_{\text{eff},2} = 1.34$. Thanks to this index matching, the reflectance (transmittance) of Bragg stacks made of such layers is low (high) and does not depend on the number of bilayers: the stacks behave as effective transparent slabs on glass substrate (Fig. 2(a)). Weak spectral oscillations are due to Fabry-Perot interferences associated with the total (stack) thickness and therefore, depend on the number of bilayers. Now, without changing porosities, we assume that all pores are filled with liquid, hence, forcing the system to switch to the colored state (Ψ_C). In practice, the Ψ_C state could be realized upon liquid infiltration through the porous network.¹³ Because pores are now filled with liquid, the index

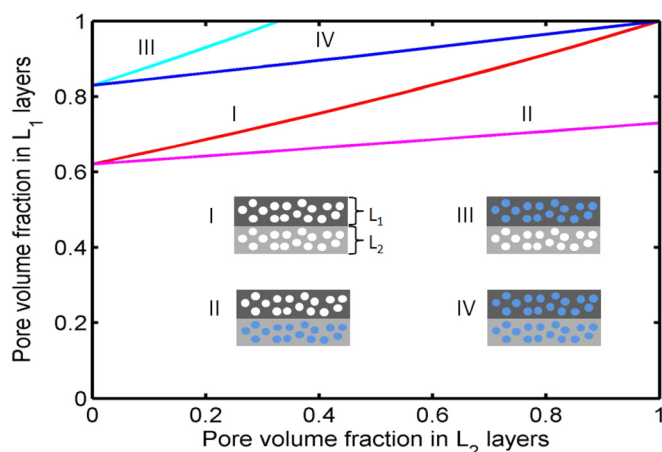


FIG. 1. Transparency master curves corresponding to mesoporous $\text{TiO}_2(L_1)/\text{SiO}_2(L_2)$ bilayers with pores (circles) either empty (white) or filled with water (blue).

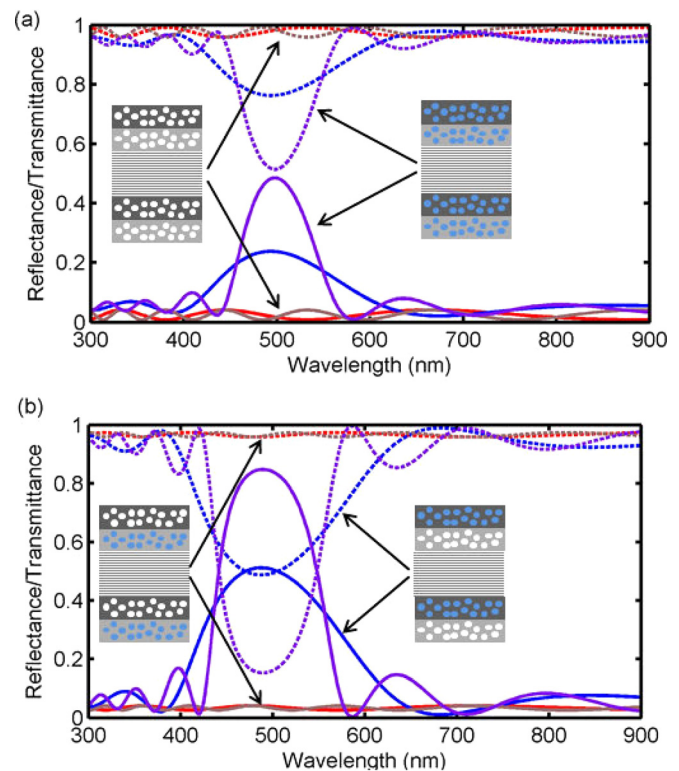


FIG. 2. Theoretical reflectance (solid curves) and transmittance (dashed curves) spectra of mesoporous $\text{TiO}_2/\text{SiO}_2$ Bragg stacks on glass substrate ($n_{\text{sub}} = 1.51$). Layer thickness: 65 nm (TiO_2) and 100 nm (SiO_2). Number of bilayers: $N = 3$ (blue and red curves) and $N = 6$ (violet and brown curves). Blue and violet (red and brown) curves correspond to (a) pore filled with water (air) in both TiO_2 and SiO_2 layers or (b) pore filled with water (air) in TiO_2 layers and air (water) in SiO_2 layers. Pore volume fractions: SiO_2 : $f_{p,2} = 0.30$ (a) and (b), TiO_2 : $f_{p,1} = 0.72$ (a) or 0.65 (b).

matching cannot be realized anymore and an effective refractive index contrast appears: $n_{\text{eff},1}=1.62$ and $n_{\text{eff},2}=1.45$. Upon switching from Ψ_T to Ψ_C states, the Bragg resonance shows up and its strength increases with the number of bilayers (Fig. 2(a)). If the Bragg resonance is tuned in the visible range (by suitably choosing layer thicknesses), the coating appears colored. Contrary to previously reported works on mesoporous $\text{TiO}_2/\text{SiO}_2$ Bragg chemical sensors,^{5–11} adsorption of the analyte (here, water) in the initially dry porous system does not result here in a shift of the Bragg wavelength (change of color) but in switching from transparency to coloration. Only recently, we reported on the fabrication of mesoporous Bragg stacks that were able to switch from transparency to coloration by infiltration of water.¹³ The present theory not only explains our previous results but also extends further the design opportunities, as detailed hereafter.

As far as hydrochromic coatings are concerned, the transmittance (or reflectance) contrast upon switching should be maximized. Our theory suggests that it is preferable to achieve the Ψ_T state with liquid-filled pores in low-index L_2 layers and empty pores in high-index L_1 layers, and the Ψ_C state being the opposite configuration. For example, keeping $f_{p,2}=0.30$ as above, we must now take $f_{p,1}=0.65$ (Fig. 1, II). The matched effective index is now $n_{\text{eff},1}=n_{\text{eff},2}=1.45$. As before, the Bragg stacks in Ψ_T state respond as effective transparent slabs though with reduced Fabry-Perot fringes due to the better index matching between the slab and the substrate (Fig. 2(b)). Upon switching from Ψ_T to Ψ_C states, the Bragg resonance is significantly stronger than before, for the same number of bilayers. This is due to the fact that higher index contrast ($n_{\text{eff},1}=1.70$ versus $n_{\text{eff},2}=1.34$) occurs with liquid-filled pores in L_1 layers and empty pores in L_2 layers. With $f_{p,1}$ and $f_{p,2}$ being related by (3), the transmittance contrast ($\Delta T = T^{\Psi_T} - T^{\Psi_C}$ at $\lambda \cong \lambda_B$) of a N -bilayer Bragg stack can be calculated as a function of the pore volume fraction in one layer, e.g., $f_{p,2}$ (Fig. 3). If, the Ψ_T state is chosen to be the configuration in which all pores of both layers are empty (Fig. 1, I), the contrast decreases with increasing $f_{p,2}$ values.

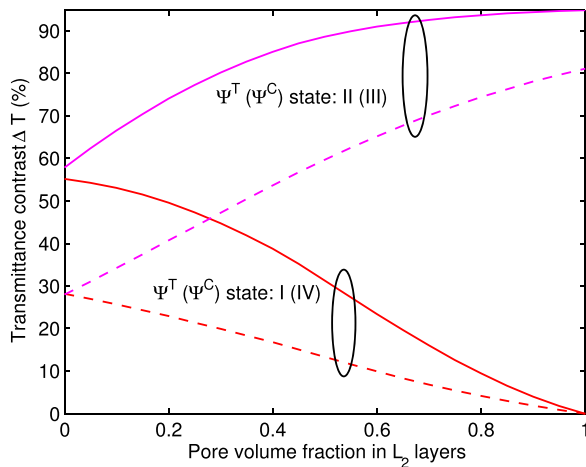


FIG. 3. Transmittance contrast ΔT upon switching from transparent to colored states as function of pore volume fraction $f_{p,2}$. Transparent state Ψ_T and colored state Ψ_C configurations are defined in Fig. 1. Pore volume fraction $f_{p,1}$ is fixed by the corresponding transparency master curve. Bragg layer stack parameters are the same as in Fig. 2. Number of bilayers: $N=3$ (dashed curves) and $N=6$ (solid curves).

The fact that the contrast drops to zero when $f_{p,2}=1.0$ is consistent with previous discussion on the corresponding transparency master curve. On the other hand, if the Ψ_T state is chosen to be the configuration with empty pores in L_1 layers and liquid-filled pores in L_2 layers (Fig. 1, II), the contrast increases with increasing $f_{p,2}$ values. The fact that higher contrasts can be achieved in this case is consistent with our previous discussion on transparency master curves. In both cases, higher contrasts can be achieved by increasing the number of bilayers.

In practical devices, it might seem extremely difficult to localize the liquid in the pores of either L_1 or L_2 layer and to displace it from one layer to the other. Solutions can, however, be found by combining surface chemistry, fluidics, and electro-wetting. Chemical surface functionalization can be used to make pores hydrophilic or hydrophobic in specific layers, and capillary attraction due to controlled pore size variations between adjacent layers can be used to promote infiltration of the liquid across the whole layer stack.¹² Electro-wetting can be used to force displacement of the liquid across adjacent layers.¹⁷

Hydrochromic coatings (deposited on glass substrate) consisting of Bragg stacks ($N=3$ bilayers) of mesoporous oxides (L_1 layers: $x\text{TiO}_2(1-x)\text{Al}_2\text{O}_3$, L_2 layers: SiO_2) were fabricated by a modified sol-gel method according a procedure described previously.¹³ The molar ratio x of mixed oxide layers was adjusted in order to fulfill the transparency condition in dry conditions (empty pores in all layers) with available porogen agents.¹³ Almost perfect matching between measured effective indexes was obtained using $x=0.6$ ($x=0.5$ used previously¹³): $n_{\text{eff},1}=1.32$ and $n_{\text{eff},2}=1.31$. Using these values, porosities equal to $f_{p,1}=0.68$ and $f_{p,2}=0.37$ were deduced from (2) with $n_{h,1}=2.13$, $n_{h,2}=1.50$, and $n_{p,1}=n_{p,2}=1.0$. The corresponding point ($f_{p,1}, f_{p,2}$) lay close to the transparency master curve (Fig. 1, I). The evolution of the color of a half-coated glass sample during successive wetting and drying steps is shown in Fig. 4. Initially, i.e., in dry conditions, the coated surface is almost transparent (Fig. 4, middle left photograph). The faint greenish color is due to slight effective index mismatch, enhanced by iridescence at non zero viewing angle. As a drop of water slips on

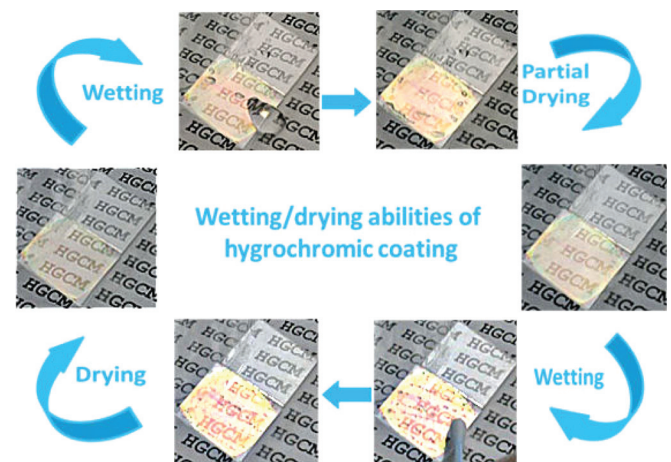


FIG. 4. Evolution of the color of a glass slide coated (half of the surface) with mesoporous oxide Bragg layer stack during successive wetting and drying steps.

the surface, the color immediately changes to orange-yellow under the streak left by the drop (Fig. 4, left top). As the water drop is further spread on the surface with a cotton stick (not shown), the orange-yellow color becomes uniform on the coated surface (Fig. 4, top right). After the sample is dried for a short time (1 min), the color fades to a faint green (Fig. 4, middle right). Transparency is not fully restored because some pores are still filled with water due to the short drying time. Re-wetting of the surface (Fig. 4, bottom) causes a color to appear again, which is slightly more yellow than during the first wetting. This result indicates the possibility to vary slightly the color by playing on the pore filling fraction. Finally, after drying for a longer time (5 min), transparency is restored. Note that the color could be more saturated by increasing the number of bilayers (here, $N = 3$).

In conclusion, we theoretically derived the general condition for achieving transparency in mesoporous layered optical media and we applied it to the switching of hydrochromic coatings from transparency to Bragg-type coloration upon displacement of water in the porous structure. The proposed concept is believed to find applications in various sensing applications and smart privacy glass windows.

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